# Thermodecomposition of *o*-benzoquinone complexes of transition metals

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Thermodecomposition of 3,5- and 3,6-di-*tert*-butyl-*o*-benzoquinone complexes of Cu, Fe, Co, Cr, Mo, and W has been investigated in the solid phase by the thermogravimetric method. The relative stability of a series of complexes has been determined from the temperatures at which their decomposition begins. Detachment of a neutral electron-donor ligand takes place in the first stage. Detachment of an *o*-quinone ligand and decomposition of the *o*-benzoquinone formed occur in the next stage. Thermodecomposition of Fe, Co, Cr, Mo, and W complexes gives oxides or carbides, while copper complexes decompose to pure metal.

**Key words:** transition metals, complexes with *o*-quinones, thermodecomposition.

The thermodecomposition of *o*-quinone homo- and hetero ligand complexes with metals of groups III, IV, V, and VI, lanthanoids, and copper,[1,2] which makes it possible to obtain metallic, metalloxide and carbide coatings, is of significant interest.

The thermostability of such complexes varies depending on the nature of the *o*-quinone and the metal and lies in the interval 100—300 °C. Complexes of 3,5-and 3,6-di-*tert*-butylbenzoquinones are the most stable. The composition of the thermodestruction products is determined mostly by the decomposition temperature of the complex.[2] Decomposition of the pyridine—*o*-quinone—copper complex in an *o*-xylene solution at 130—165 °C proceeds with the formation of pyridine, copper powder, and 3,5-di-*tert*-butylbenzoquinone, which, yields 3,5-di-*tert*-butylpyrocatechol and other products of quinone degradation free of carbonyl under the reaction conditions.[3] In the authors' opinion the mechanism of thermodecomposition involves the consecutive elimination of pyridine and *o*-quinone ligands with the intermediate formation of copper catecholate, which is less stable than the initial complex. In the products of decomposition of the tris(semiquinone)chromium complex, the metal, isobutylene, and a mixture of pyrocatechols were found.[2]

In the present work the solid-phase thermodecomposition of 3,5- and 3,6-*o*-quinone complexes of Cu, Fe, Co, Cr, Mo, and W was studied by the thermogravimetric method. Table 1 lists the temperatures of the initiation of decomposition $T_0$, the temperatures of the maximum decomposition rate $T_1$, $T_2$, $T_3$, mass losses in first step $M_I$, final mass losses $M_f$, and theoretical predictions of mass losses assuming decomposition of the complex yields metal and metal oxide. As follows from Table 1, the temperatures of the initiation of decomposition lie in the interval 100—200 °C. The presence of several peaks on the DTG curves points to a multistep decomposition. For the hetero ligand complexes, the mass loss in the first step usually corresponds to the mass of a neutral donor ligand. Comparison of the

**Table 1.** Thermogravimetric analysis data

| Compound | $T_0$ | $T_1$ | $T_2$ | $T_3$ | $M_I$ | $M_f$ | $M_{met}$ | $M_{ox}$ |
|---|---|---|---|---|---|---|---|---|
| $[Cu(3,5\text{-}DBCat) \cdot Py]_4$ | 90 | 120 | 210 | 295 | 25.0 | 82 | 82 | 78 |
| $Cu(3,6\text{-}DBSQ)_2 \cdot Py$ | 90 | 115 | 200 | 310 | 23.1 | 91 | 89 | 86 |
| $[Cu(3,5\text{-}DBCat) \cdot Dipy]_2$ | 160 | 180 | 220 | 440 | 38.0 | 87 | 85 | 82 |
| $Cu(3,5\text{-}DBCat) \cdot Et_3N \cdot EtOH$ | 75 | 100 | 170 | 280 | 19.0 | 79 | 83 | 79 |
| $Fe(3,6\text{-}DBSQ)_2 \cdot Dipy$ | 210 | 250 | 340 |  | 56.0 | 87 | 91 | 88 |
| $Cu(3,5\text{-}DBSQ)_2$ | 100 | 185 | 240 | 345 |  | 84 | 87 | 84 |
| $Fe(3,6\text{-}DBSQ)_3$ | 150 | 220 | 330 |  |  | 54 | 92 | 89 |
| $Mo(3,5\text{-}DBSQ)_3$ | 200 | 280 | 470 |  |  | 82 | 87 | 84 |
| $Co(3,6\text{-}DBSQ)_2$ | 130 | 200 | 310 | 370 |  | 80 | 88 | 83 |
| $W(3,5\text{-}DBSQ)_3$ | 225 | 280 | 485 |  |  | 75 | 78 | 75 |
| $Cr(3,5\text{-}DBSQ)_3$ | 200 | 235 | 330 |  |  | 84 | 92 | 89 |

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values of the final mass losses with those theoretically predicted (assuming the decomposition products are metals or metal oxides) shows that copper is the product of the decomposition of the copper complex and metal oxides or carbides are the products in case of the other complexes (see Ref. 4). Taking the temperature of the initiation of decomposition as the thermostability parameter, all of the *o*-semiquinone metal complexes can be arranged in the following order (see Ref. 2): Cu < Co < Fe < Cr < Mo ≤ W.

Thermodecomposition of copper 3,5-di-*tert*-butylcatecholate $[Cu(3,5\text{-}DBCat) \cdot Py]_4$ proceeds in three stages, each having the following parameters: temperature interval (70—150, 150—280, and 280—350 °C, respectively); maximum decomposition rate (120, 210, and 300 °C, respectively); mass losses (25, 55, and 2 %, respectively) (Fig. 1). In the third stage at 305 °C, an exo-effect is observed on the DTG curve. The first and second thermodecomposition stages are not observed in this curve or have a slight endo-effect. The kinetic parameters of the process were determined by Freeman—Carol's method and by taking the double logarithm.[5] The first step of the thermodecomposition of *o*-quinone complexes follows zero-order kinetics and the second step follows first-order kinetics.

Solid-phase decomposition of $[Cu(3,5\text{-}DBCat) \cdot Py]_4$ (**1**) in evacuated ampules at 70, 150, 210, and 300 °C with freezing-out of the volatile products was used to investigate the thermodecomposition products. The results of GLC analysis of the products that escaped the heating zone are listed in Table 2. As can be seen, at 70 °C toluene is eliminated and elimination of pyridine starts. Toluene was used as the solvent for the synthesis of the complex and seems to be incorporated in the crystalline lattice of the complex. The yield of toluene is 0.2—0.3 mole per mole of starting compound. The IR spectrum of the solid residue coincides with that of the starting compound.

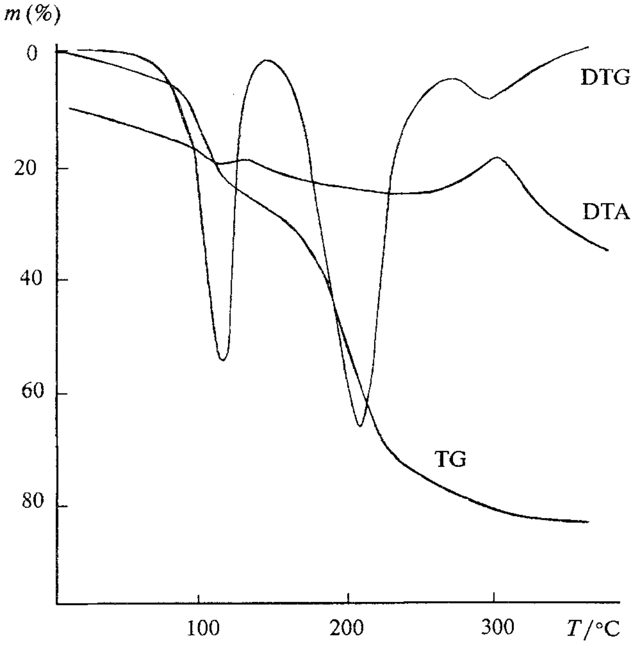

**Fig. 1.** The derivatographic curve of $[Cu(3,5\text{-}DBCat) \cdot Py]_4$, heating rate 6 deg · $min^{-1}$.

**Table 2.** The composition of the products of thermodecay (in moles per mole of the complex)

| $T$/°C | τ/h | Quinone | Pyridine | Toluene | Isobutylene | Pyrocatechol | Phenol |
|---|---|---|---|---|---|---|---|
| 70 | 2 | — | 0.07 | 0.21 | — | — | — |
| 150 | 2 | Traces | 0.83 | 0.24 | — | — | — |
| 210 | 2 | 0.17 | 0.96 | 0.24 | 0.25 | Traces | Traces |
| 300 | 2 | 0.13 | 0.74 | 0.21 | 0.44 | Traces | Traces |
| 420 | 1 | 0.01 | 0.89 | 0.25 | | Traces | Traces |
| 460 | 1 | 0.05 | 1.00 | 0.30 | | Traces | Traces |

Complete elimination of pyridine and toluene occurs at 150 °C, which corresponds to the TGA data. 3,5-Di-*tert*-butylbenzoquinone is detected in trace amounts. No metallic copper was formed, which suggests the formation of Cu(3,5-DBCat). The IR spectrum of the solid residue contains bands characteristic of Cu(3,5-DBCat).[6] The zero-order kinetics of this stage may testify that there are no basic skeletal changes in the complex.[7] Like the majority of 3,5-disubstituted quinone metal complexes, Cu(3,5-DBCat) is associated. The temperature of complex destruction is above 150 °C, which coincides with the temperature given[6] for Cu(3,5-DBCat). Thus, when the initial complex is heated at 150 °C for 2 h, the copper catecholate complex can be obtained in a good yield. This complex is fairly difficult to obtain in a pure form by other methods.

Complete decomposition of copper complexes occurs at 210 °C over 2 h, which is confirmed by calculations using rate constants obtained by thermogravimetry. After 2 h the degree of conversion of **1** is 99 %.

As can be seen from Table 2, thermodecomposition of **1** at 210 °C yields 0.2 mole of 3,5-di-*tert*-butylbenzoquinone. At this step, even a slight deviation of temperature from 210 °C results in a drastic increase or decrease in the yield of quinone due to its decomposition. The decomposition products contain traces of 2,4-di-*tert*-butylphenol and 3,5-di-*tert*-butylpyrocatechol. The gas phase contains 0.25 mole of isobutylene. The solid residue contains 0.9 mole of metallic copper, which forms a mirror on the walls of the ampule and is also mixed with tar. GLC analysis revealed that this tar contains small amounts of 3,5-di-*tert*-butylbenzoquinone, 3,5-di-*tert*-butylpyrocatechol, and a number of unidentified products. The IR spectrum of a tar extract contains bands at 3480 and 3550 $cm^{-1}$ due to OH groups linked with an aromatic ring, and bands at 1730 and 1765 $cm^{-1}$ due to carbonyls bound with an oxygen-containing cycle. The formation of isobutylene and 3,5-di-*tert*-butylpyrocatechol is caused by decomposition of 3,5-di-*tert*-butylbenzoquinone at 210 °C, which has been shown in a separate experiment. However, 2,4-di-*tert*-butylphenol and carbonyl-containing products with IR bands at 1730 and 1765 cm$^{-1}$ are absent from the quinone thermodecomposition products. The formation of 2,4-di-*tert*-butylphenol during thermodestruction of **1** shows that under the decomposition conditions redox disproportionation of *o*-quinone catalyzed by the copper complex occurs along with its destruction. The same reactions may be responsible for the formation of lactone-like products having IR bands at 1730 and 1765 cm$^{-1}$ similar to those obtained earlier.[8,9]

The reaction at 300 °C gives the same products with a higher yield of isobutylene. X-ray analysis of the solid residue showed that it contains metallic copper without any admixtures of copper oxide or carbide. The exo-effect on the DTA curve is caused by the sublimation of tar at this temperature.

The data obtained allows us to propose the following mechanism of thermodestruction of *o*-quinone metal complexes. The first step, in the case of hetero ligand complexes, is the elimination of a neutral electron-donor ligand, the second step is the elimination of an *o*-quinone ligand and the destruction of the *o*-quinone formed. Thermodecomposition of Fe, Co, Cr, Mo, and W complexes yields oxides or carbides, and copper complexes give metallic copper.

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